

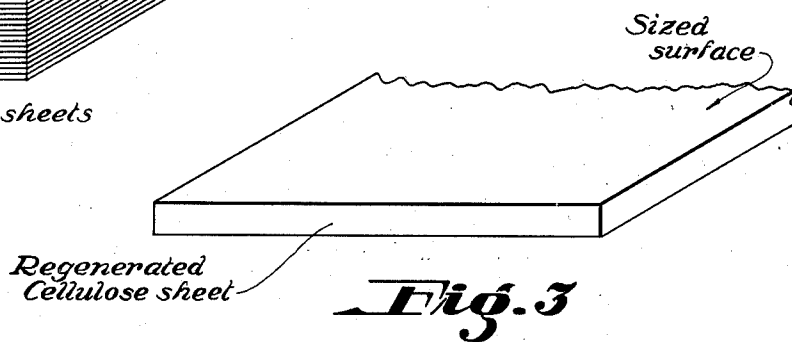
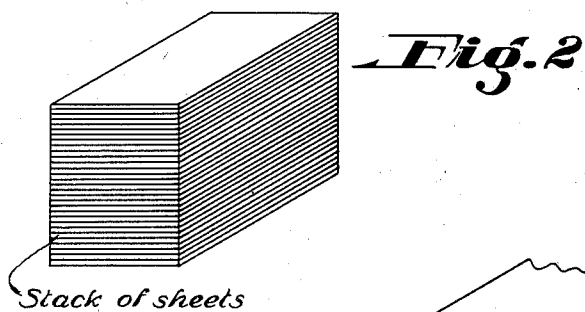
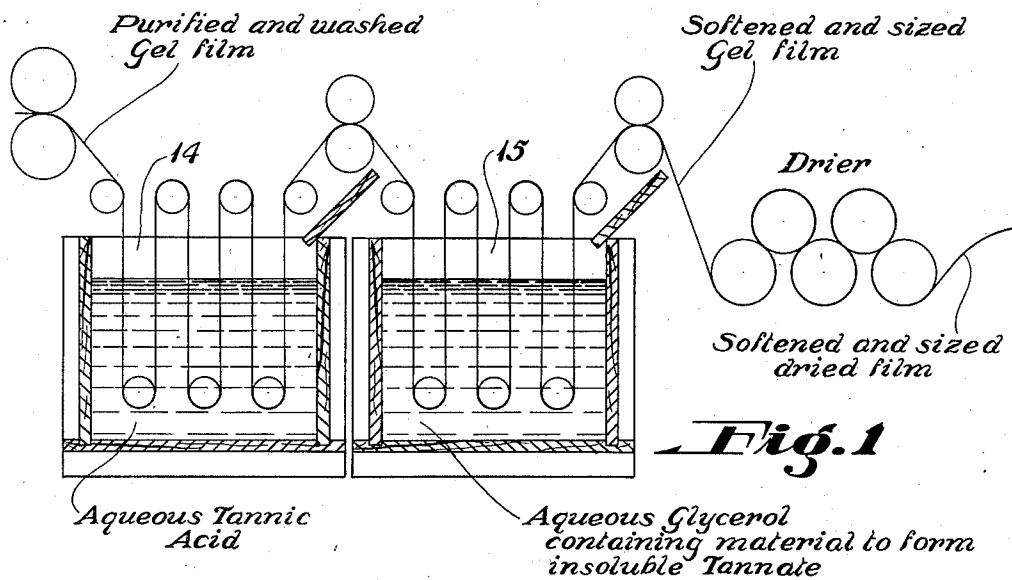
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SIZED PELLICLE

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SIZED PELLICLE

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This invention relates to non-fibrous pellicles, and it more particularly pertains to improved thin, flexible, sheets and films of regenerated cellulose.

Thin, flexible regenerated cellulose pellicles are prepared commercially by coagulation and regeneration, followed by purification, impregnation of the wet or gel film with an aqueous solution of a suitable softener, usually glycerol, the softened film then being dried. Such film is designated in the trade as plain film, as distinct from those varieties which are given a subsequent treatment, such as a lacquering treatment to impart a coating, such as a moistureproofing coating.

Commercial, thin, flexible, plain regenerated cellulose pellicles usually contain, when manufactured, 5% to 8% moisture and 9% to 15% softener, these percentages being based on the weight of the dry cellulose. The softener, e. g., glycerol, having a very low volatility, remains practically unchanged in concentration in the sheet over a long period of time. The moisture content in the sheet, however, is subject to wide and sometimes rapid fluctuations depending on the moisture content of the air to which the sheet is exposed.

It is most desirable that thin, regenerated cellulose sheeting be properly softened, that is, flexible and durable, under a wide variety of atmospheric conditions. In an atmosphere of medium to high relative humidity such film is found to have adequate durability and flexibility if it contains from 9% to 15% glycerol, based on the dry weight of the cellulose. In atmospheres of low relative humidity such as obtains in dry climates and in the cold weather of the northern climates, thin, regenerated cellulose film containing from 9% to 15% glycerol becomes quite fragile, due to the loss of a substantial amount of contained moisture, and it has been suggested that in order to overcome this difficulty the glycerol content be greatly increased in order to insure the retention of an adequate amount of moisture in the film.

However, the increase of the glycerol contained in the film to an amount substantially in excess of 15%, based on the weight of the dry cellulose, is impractical for certain reasons. For example, thin, plain transparent regenerated cellulose films are very smooth and pliable and when such films are stacked in cut sheets on one another or wound tightly on rolls air is expelled from between the sheets, causing great difficulty in separation thereof. In addition, the high content of softener imparts relatively great surface tackiness and tendency towards cohesion of adjacent

sheets. Even when the glycerol content is 15%, precautions must be taken to prevent absorption of too much moisture, such precautions being, for example, the storing of the stacked sheets or rolls in a properly humidified room, wrapping with moistureproof material during storage, avoiding long periods of storage, storing under as little pressure as possible, etc. It will be understood, in this discussion, that increased moisture content generally increases the tendency towards tackiness of the surface of the sheet. It has previously been proposed to deposit on such thin, flexible regenerated cellulose sheets a substantially invisible layer of very fine solid particles of inorganic material, in order to increase surface slip and sticking resistance. However, films so treated exhibit less affinity for the usual aqueous adhesives used to bond such films to themselves, as in the making of bags, and to other materials, such as paper labels, the strength of the adhesive bond at seams and closures of articles made from such films being very weak. The reason for the decreased receptivity towards adhesives of films treated with such deposits which have been applied for the purpose of improving slip probably lies in the fact that the water in the aqueous adhesive has difficulty in penetrating the thin surface layer of the size.

In addition, proposed methods for applying sizes to thin, regenerated cellulose film are generally characterized by application of the size from an aqueous bath prior to the drying of the film; the choice of sizing materials is thus limited to those which are soluble or dispersible in aqueous media, and which will not be adversely affected by the heat of the drying operation. In addition, since the film at this point is in the gel state, a certain amount of the sizing material may penetrate to the interior of the film where it serves no useful purpose as far as slip is concerned, and such penetration may adversely affect the transparency and appearance of the sheet.

It is an object of this invention to produce a new and useful thin, flexible film having good slip characteristics. Another object comprehends the production of new and useful thin and flexible films comprising a substantially non-fibrous, non-porous material, such as regenerated cellulose having improved resistance to breaking when subjected to low humidities, for example, during cold weather. A further object of this invention pertains to improvement in the sticking resistance of thin, flexible cellulosic film. Another object comprises the production of thin, 55

flexible film of high sticking resistance, having also improved receptivity for aqueous adhesives. It is a still further object to provide improved means for sizing such non-fibrous, non-porous material. Other objects of the invention will appear hereinafter.

In general, the objects of this invention are attained by the formation of insoluble salts of tannic acid upon the surface of the regenerated cellulose film. Optionally, other insoluble materials such as finely divided clays, and certain wetting agents well known to the art may also be included in the sizing layer of the cellulose film. Such a layer may be applied to one or both sides of the film.

From the following description and specific examples, in which are disclosed certain embodiments of the invention as well as details of what is believed to be the best mode for carrying out the invention, it will be apparent how the foregoing objects and related ends are accomplished. The written description is amplified by the accompanying drawing, in which:

Figure 1 is a diagrammatic sectional elevation view illustrating the apparatus for handling transparent film according to the present invention;

Figure 2 is an isometric view illustrating a stack of sheets of regenerated cellulose film prepared according to the present invention; and

Figure 3 is a greatly exaggerated perspective view illustrating a single sheet of regenerated cellulose.

Referring now to the details of the drawing, the numerals 14 and 15 indicate treating tanks of the conventional type found in viscose regenerating machines, for example, those of U. S. A. Patent No. 1,548,864 (Brandenberger). As will be clear from the legends in Figure 1, the purified and washed gel film as received from the regenerating, desulfuring, bleaching and other preliminary treatment sections of the casting machine, passes about rollers through an aqueous solution of tannic acid in tank 14, after which it is squeezed to remove excess solution, and then passes into the softening bath which contains material to form an insoluble tannate with the tannic acid already associated with the film. From this bath the film passes to a drier for drying, after which it may be collected in mill rolls. The finished material may be cut to size and stacked, as indicated in Figure 2. Because of the presence of the tannate, the adjacent sheets of the stack exhibit no tendency to stick to each other.

The pellicles prepared are perfectly transparent, so that the sizing material is not apparent to the eye, but a greatly enlarged view of a single sheet is shown in Figure 3 in order to illustrate the invention. A legend on the drawing indicates that the surface is sized.

The invention will be described with specific reference to thin pellicles of regenerated cellulose, such as are suitable for use as wrapping tissue, although it is to be understood that the invention may be likewise applied to the production of other thin pellicles of materials other than regenerated cellulose. The following examples illustrate various embodiments of the invention.

Example I

A thin, plain, transparent regenerated cellulose pellicle having a thickness when dry of about 0.0009 inch, after usual purification and washing treatments, is passed through a solu-

tion containing .1% tannic acid and next through a solution of glycerol and .02% of calcium chloride. The excess solution is removed by means of squeeze rolls and the film dried in the conventional manner.

Example II

A film of the same composition and character as that of Example I, after purification and washing, is passed through a .1% solution of tannic acid and then through a solution of glycerol and .07% zinc acetate which is made up on the basis of the crystallized salt $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$. As in Example I, the excess solution is removed by means of squeeze rolls and the film dried in the conventional manner.

Example III

The film of Example I is passed first through a .1% aqueous solution of sodium tannate and then through an aqueous solution containing glycerol and .03% of the zinc acetate salt of Example II. The film, after drying, is of good appearance and transparency, has high sticking resistance, and gives an exceptionally good gluing bond with aqueous adhesives.

Example IV

A thin, flexible regenerated cellulose pellicle, after purification and washing, is passed through an aqueous solution of .22% tannic acid and then through a solution of glycerol and .18% calcium acetate, based upon the crystallized salt $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$. As before, the excess solution is removed by means of squeeze rolls and the film dried in the conventional manner.

Example V

A thin, flexible, regenerated cellulose film, after purification and washing, is passed through a solution of .22% tannic acid and then through a solution of glycerol and .18% calcium acetate in which is suspended .037% of bentonite. The film is dried as before.

Example VI

A thin, flexible regenerated cellulose film, after purification and washing, is passed through an aqueous solution of .23% sodium tannate and then through a solution containing glycerol, .18% magnesium sulfate, determined on the basis of the tetrahydrate. The film is then dried in the conventional manner.

Example VII

A thin, flexible regenerated cellulose film, after purification and washing, is passed through a solution of .23% sodium tannate and then through a solution containing glycerol, .18% magnesium sulfate, and a suspension of .15% bentonite. The film is then dried in the conventional manner.

Example VIII

A thin, flexible regenerated cellulose film, after washing and purification, is passed through a .1% aqueous solution of sodium tannate and then through a solution containing glycerol, .1% of magnesium sulfate heptahydrate, .15% bentonite and .002% of sodium lauryl sulfate. Excess liquid is removed by means of squeeze rolls and the film dried in the conventional manner.

Example IX

A thin, flexible regenerated cellulose film,

after purification and washing, is passed through a .15% aqueous solution of sodium tannate and then through a solution containing glycerol, .15% aluminum sulfate, based on the salt of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. After removal of excess liquid by means of squeeze rolls, the film is dried in the conventional manner.

Example X

A thin, flexible regenerated cellulose film, after purification and washing, is passed through an aqueous solution of .15% sodium tannate and then through a solution containing glycerol, .15% aluminum sulfate, .15% bentonite and .002% sodium lauryl sulfate. The film is then dried in the conventional manner.

Each of the sized pellicles prepared according to each of the foregoing examples is perfectly transparent, and even after several days, exhibits no substantial tendency to stick when stacked on each other in an atmosphere of 80% relative humidity, at 25° C. and under a pressure of one pound per square inch, the sheets being 6 inches square. Additionally, the films prepared according to the above examples show an affinity towards aqueous adhesives comparing favorably with that of unsized sheets of the same material and thickness.

According to the invention, the anti-sticking agents are applied to transparent regenerated cellulose sheets either before, during, or after impregnation of the softener in such a manner that practically no impairment in the appearance or performance of the dried product results. Preferably, the insoluble salt of tannic acid is formed in situ upon the surface of the sheet by first impregnating the sheet with a soluble salt of tannic acid or tannic acid itself and subsequently treating the impregnated film with a solution of a soluble salt of a cation which will precipitate an insoluble tannic acid salt. Obviously, the reverse procedure may be used, that is, the initial impregnation of the prepared film with a solution of a salt of the desired cation and subsequent treatment of the impregnated film with tannic acid or a soluble tannate. The softener may advantageously be placed in the second treatment bath. Before entering the drier, the excess anti-sticking agent, together with the excess softener solution, may be removed by suitable squeeze rolls, scraper rods, or doctor knives, or the like. The amount of anti-sticking agent which is applied is controlled by adjusting the concentration of the anti-sticking agent in the treating baths, or by varying the amount of excess removed. If it is desired to apply the anti-sticking agent separately, the pellicle may be treated with a softener bath, the excess removed, as indicated above, and then the solution or solutions of the appropriate treating agents are applied by means of sprays, dip rolls, etc. It is preferred not to immerse the softener treated pellicle in a separate treating bath containing only the reagents forming the anti-sticking agent since part of the softener would be removed from the pellicle. If it is desired, the insoluble tannate sizes may be applied to the film as aqueous dispersions from treatment baths, sprays, dip rolls, etc. For this purpose, the addition of suitable dispersing agents such as triethanolamine, soluble soaps, etc., may be made.

Preferably, only very minute quantities of anti-sticking substances are applied to the

transparent regenerated cellulose pellicles, which substances, after drying of the pellicle, will usually and preferably amount to less than 2% of the product and may even amount to as little as a few hundredths of a per cent.

In carrying out the sizing treatment, it is essential that the dispersion or solution be so prepared, that the quantity be so controlled, and that drying be so carried out that the final product is substantially not inferior to similar unsized products, particularly in retention of transparency, in brilliance and in receptiveness of the usual aqueous adhesive.

Generally speaking, the process is best applied to pellicles in the gel state, that is, as they are obtained in the course of manufacture in the purified and washed but undried state. However, it is possible to apply the principles of this invention to pellicles which have been dried, by subjecting them to a rewetting step during or prior to the treatment afforded by the present invention. Obviously, it is much more economical and practical to work with the pellicle in the gel state. Although transparent pellicles are to be preferred, it is within the scope of the invention to use pigmented, colored, or otherwise decorated pellicles. The process, furthermore, does not interfere with subsequent treatments including lamination, coating, gluing, or the like. Thus, the products of this invention may be provided with surface coatings as, for example, moistureproof surface coatings without harmful effects due to the treatment according to this invention.

Inasmuch as the tannates are precipitated by calcium, magnesium, and similar salts, it is preferable to use soft water in preparing the treating bath. Furthermore, it is preferred that the pellicle to be treated should be washed with soft water before being introduced into the treating bath. This last is particularly true when the process is carried on in a continuous manner, for if hard water is used for washing and is not removed prior to the sizing treatment, the carry-over by the pellicle will gradually cause a precipitation of tannates in the treating bath.

The tannates which are used in accordance with this invention are all classed as insoluble; that is, they have a solubility in water of less than 5% at ordinary temperatures and include the species calcium, barium, strontium, zinc, magnesium, cadmium and aluminum tannate. It is also preferred that the tannates used as sizing agents in the practice of the invention be substantially colorless. In general, the tannates used as sizing agents in accordance with this invention are formed during the process by reacting, upon the film, solutions of soluble tannates or tannic acid, (such as, for example, tannic acid itself, sodium tannate, potassium tannate, cesium tannate, or other soluble salts of tannic acid) with solutions of soluble salts containing as a cation calcium, barium, strontium, aluminum, or other materials giving insoluble salts of tannic acid. Such soluble salts include calcium acetate, calcium chloride, barium chloride, magnesium sulfate, strontium sulfate, strontium acetate, zinc acetate, cadmium acetate, aluminum sulfate.

If desired, mixtures of the tannate sizing agents may be used. Additionally, the tannate sizing agents may be applied in admixture with other sizing materials, for example, argillaceous materials such as bentonite, china clay and aluminum silicate.

The invention in its preferred form contemplates the use of glycerol as the cellulose softener. It is to be understood, however, that any water-soluble, substantially non-volatile cellulose softener may be used, such as diethylene glycol, triethylene glycol, invert cane sugar, glucose, sorbitol, calcium chloride, triethanolamine, carbamide, etc., or suitable combinations of such softeners. The invention is independent, however, of the type of softener used, and indeed, relatively volatile softeners may be used or the softener may be omitted if occasion demands.

The use of these insoluble tannates not only gives great stick resistance of the film so treated but likewise, provides a film for which adhesive bonds of great strength may be obtained with the ordinary aqueous adhesives. In some cases, the adhesive bond may be further improved by the incorporation of a wetting agent in the treatment bath and consequently, upon the surface of the pellicle which will aid in the penetration of the adhesive to the base sheet. Wetting agents which may be used for this purpose are soluble soaps such as potassium stearate, sodium stearate, triethanolamine stearate, Monopol oil, sodium ricinoleate, and water-soluble salts (particularly the sodium salts) of the half esters of sulfuric acid and alcohols in which the aliphatic radical contains at least 8 and preferably 12 to 18 carbon atoms, such as sodium lauryl sulfate, sodium myristyl sulfate, sodium acetyl sulfate, sodium oleyl sulfate and sodium stearyl sulfate. Mixtures of these wetting agents are sometimes preferred.

Thin, flexible sheets of the kind referred to, when sized with materials of this invention, show very great resistance to sticking and caking when stacked and stored under pressure. It is furthermore apparent that a sizing or anti-sticking agent which will improve the sticking resistance of regenerated cellulose pellicles and at the same time permit the pellicles to remain receptive to aqueous adhesives which are satisfactory for use with untreated pellicles constitutes an outstanding contribution to the art. Needless to say, there are many uses to which cellulosic pellicles of the type described may be put wherein the anti-sticking characteristic is of major import while the receptivity to aqueous adhesives is of little concern. In such cases, a pellicle having improved sticking resistance, regardless of its receptivity to aqueous adhesives, will be useful and the production of such pellicles is well within the scope of the present invention.

Also, adhesion of printing inks to surfaced transparent regenerated cellulose pellicles is often greatly impaired except where the glueable compositions of the present invention are employed.

One very practical feature of the process of this invention is that it may be carried out with no appreciable increase in cost or without any alteration in the machines usually used for producing transparent regenerated cellulose sheets or in the method for subsequent handling by the manufacturer, converter, or consumer.

The highly softened cellulosic sheets represent a further increase in utility since they are much more durable at freezing temperatures than the usual commercial product.

It is obvious that these anti-sticking substances may be applied with great advantage to transparent regenerated cellulose sheets containing the usual quantity of softening agent, especially when such products are to be used in territories of high atmospheric humidity, to overcome the at-

mospheric sticking of adjacent sheets by absorption of moisture.

Percentages, parts and proportions referred to to herein are intended to be percentages, parts and proportions by weight, unless otherwise specified.

Any variations or modifications of the invention as described above which conform to the spirit of the invention are intended to be included within the scope of the claims.

I claim:

1. A thin, flexible, non-fibrous pellicle containing a deposit on a surface thereof of a water-insoluble tannate in an amount sufficient to prevent sticking at 25° C. and 80% relative humidity under a pressure of one pound per square inch but insufficient to substantially impair the transparency of the coating.

2. A thin, flexible, non-fibrous regenerated cellulose pellicle containing a deposit on a surface thereof of a water-insoluble tannate and bentonite.

3. A thin, flexible, regenerated cellulose pellicle containing a deposit on a surface thereof of a water-insoluble tannate in an amount sufficient to prevent sticking at 25° C. and 80% relative humidity under a pressure of one pound per square inch.

4. A thin, flexible, non-fibrous regenerated cellulose pellicle containing a deposit on a surface thereof of a water-insoluble, substantially colorless tannate and bentonite.

5. A thin, flexible, regenerated cellulose pellicle containing a deposit on a surface thereof of aluminum tannate.

6. A thin, flexible, regenerated cellulose pellicle containing a deposit on a surface thereof of aluminum tannate and bentonite.

7. A thin, flexible, regenerated cellulose pellicle containing a deposit on a surface thereof of a tannate of the group consisting of calcium tannate, zinc tannate, aluminum tannate and magnesium tannate.

8. A thin, flexible, regenerated cellulose pellicle containing a deposit on a surface thereof of a tannate of the group consisting of calcium tannate, zinc tannate, aluminum tannate and magnesium tannate and bentonite.

9. The process of improving surface characteristics of a thin, flexible, non-fibrous pellicle which comprises imposing on a surface of said pellicle a water-insoluble tannate in an amount sufficient to prevent sticking at 25° C. and 80% relative humidity under a pressure of one pound per square inch but insufficient to substantially impair the transparency of the coating.

10. The process of improving surface characteristics of a thin, flexible, non-fibrous regenerated cellulose pellicle which comprises imposing on a surface of said pellicle a water-insoluble tannate and argillaceous sizing material from the group consisting of bentonite, china clay and aluminum silicate.

11. The process of improving surface characteristics of a thin, flexible, regenerated cellulose pellicle which comprises imposing on a surface of said pellicle a water-insoluble tannate and argillaceous sizing material.

12. The process of improving surface characteristics of a thin, flexible, non-fibrous pellicle which comprises imposing on a surface of said pellicle aluminum tannate.

13. The process of improving surface characteristics of a thin, flexible, non-fibrous pellicle

which comprises imposing on a surface of said pellicle a tannate of the group consisting of calcium tannate, zinc tannate, aluminum tannate and magnesium tannate.

5 14. The process of claim 17 characterized in that the insoluble tannate is formed in situ on the surface of the pellicle.

10 15. The process of claim 18 characterized in that the insoluble tannate is formed in situ on the surface of the pellicle.

16. The process of claim 11 characterized in that the insoluble tannate is formed in situ on the surface of the pellicle.

13 17. The process of improving surface characteristics of a thin, flexible, non-fibrous pellicle which comprises imposing on a surface of said pellicle aluminum tannate and bentonite.

20 18. The process of improving surface characteristics of a thin, flexible, non-fibrous pellicle which comprises imposing on a surface of said pellicle a tannate of the group consisting of calcium tannate, zinc tannate, aluminum tannate, magnesium tannate, and bentonite.

19. The process of improving surface characteristics of a thin, flexible, regenerated cellulose pellicle which comprises imposing on a surface of said pellicle a water-insoluble tannate and clay.

5 20. The process of improving surface characteristics of a thin, flexible, regenerated cellulose pellicle which comprises imposing on a surface of said pellicle a water-insoluble tannate and bentonite.

10 21. The process of claim 11 characterized in that the insoluble tannate is formed in situ on the surface of the pellicle in the presence of a wetting agent.

22. The process which comprises passing a 15 thin, flexible, purified and washed regenerated cellulose gel film through an aqueous solution of .15% sodium tannate, then through a solution containing glycerol, .15% aluminum sulfate, .15% bentonite and .002% sodium lauryl sulfate, 20 and thereafter drying the film.

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